Removal of Chlorides from Waste Incineration Residues

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Summary
Chlorides were removed from the medical waste bottom ash and the municipal solid waste incineration fly ash samples using washing/leaching procedure. The treatment procedures as well as mineralogical phase analysis of raw and washed/leached samples were discussed. Pozzolanic/hydraulic properties of samples were determined and discussed in relationship to bottom ash/fly ash utilization.

Keywords: medical waste bottom ash; MSWI fly ash; chlorides washing; mineralogical phase analysis

Introduction

Incineration of waste has many advantages including a complete disinfection, considerable reduction in volume (up to 90%) and energy recovery (waste to energy system) [1]. Waste incineration, however, is not a final solution as it generates secondary wastes, especially bottom and fly ashes, that must be afterwards disposed [2]. Bottom ash is reported as less polluted than fly ash [3] and it was only recently included (2003) on the list of dangerous waste materials according to the Council of the European Union. While fly ash has already found the place on the list of dangerous waste materials with code 19.01.13. Previous studies have shown that bottom ash from municipal solid waste (MSW) incineration might be a valuable resource and can be used as a construction material [4]. Due to the fact, that chemical composition of the MSW bottom ash and the medical waste (MW) bottom ash is similar, the MW bottom ash may be utilized in the same way [5]. Nevertheless both, MW bottom ash and MSWI fly ash contain high concentrations of leachable toxic metals (i.e., As, Cd, Cr, Cu, Ni, Pb, and Zn) and soluble components (particularly chloride salts) [6, 7], therefore their pre-treatment prior to landfilling or utilization is necessary [8, 9].

High levels of chloride salts present in MW bottom ash and MSWI fly ash are harmful not only during the recycling process but also during their application as a possible resource in the construction industry. Chloride compounds like halite (NaCl) and sylvite (KCl) are easily released in leaching tests and can cause a major problem to environment and during the concrete production as well as serious corrosion problems in the cement kiln [10]. A number of treatment methods for the chloride salts reduction have been suggested, such as washing/leaching with water and/or acids [11, 12].

This paper summarizes the results of research aimed at studying the possibilities of chloride salts removal from the MW bottom ash and MSWI fly ash using water and acid leaching pretreatment for the potential use of this material in construction industry.

Materials and methods

Bottom ash. Bottom ash (BA) sample was collected from the medical waste incineration plant located in the Czech Republic. This plant uses discontinuous ventricular pyrolysis furnace with a flue gas extension chamber. It utilizes primarily a hazardous infectious waste from medical facilities, including discarded pharmaceuticals and veterinary waste.

Fly ash. Fly ash (FA) samples were collected from incineration plants located in Austria. They are referred in the text as samples 1, 2 and 3. Sample 1 was collected from the MSW incineration plant using the following technology: grate furnace, dry flue gas cleaning system, bag house

Tab. 1. Water leachate analysis of the MW bottom ash and the MSWI fly ash at S/L = 1/10

Tab. 1. Analiza wody z odcieku z popiołu dennego odpadów medycznych (MO) oraz popiołu lotnego ze spopielenia miejskich odpadów stałych (MOS) na poziomie S/L = 1/10

Sample		**pH**	**Conductivity**	**Dissolved solids**	**Cl^-**	**$(SO_4)^{2-}$**
			mS/cm	mg/l	mg/l	mg/l
Fly ash	**1**	10.64	39.00	30925	10 104	2 320
	2	11.63	29.80	19495	8 965	1 150
	3	9.43	6.48	4055	1 492	668
Bottom ash		11.91	28.70	17503	8423	240

filter. Sample 2 was acquired from the MSW incineration plant using the following technology: grate furnace, electrostatic precipitator. Finally, Sample 3 was collected from the refused derived fuel and sewage sludge incineration plant using the following technology: fluidized bed combustor, electrostatic precipitator. FA samples were collected from the air pollution control device and homogenized in the laboratory. Consequently, samples were prepared for analyses using the quartering method.

Chlorides washing/leaching. For the chlorides removal, simple distilled water washing in the 24 hours period was used, with a 1/10 solid/liquid phase ratio. For more efficient chlorides removal, the 3 hours leaching procedure was used. During the first two hours the MW bottom ash was leached with distilled water followed by one hour leaching with 1M H_2SO_4 (S/L = 1/10, pH = 1.4). Chloride concentration analysis (dry mass) was determined using X-ray fluorescence (XEPOS III HE, Spectro) according to CSN EN 15309 - Characterization of waste and soil - Determination of elemental composition by X-ray fluorescence. The analysis was conducted in the accredited laboratory ZUOVA Ostrava, CZ.

Mineralogical phase analysis. A powder X-ray diffraction analysis was used to identify the mineralogical phases of the raw and washed/leached fly ash and bottom ash samples. The analysis was conducted using a Bruker-AXS D8 Advance diffractogram equipped with a silicon strip detector LynxEye. The following scan parameters were selected for each test: 5–80° 2θ angle range, 0.014° 2θ step width, 0.25 s step time, and 3-5 measurements. Data were recorded digitally. Peak positions and intensities were qualitatively identified using the peak search software Bruker – AXS Diffrac., resp.-Diffrac. EVA and the PDF 2/JCPDS (2011 version) database as a source of reference data. Quantitative phase analysis was conducted using Bruker Topas programme, version 4.2, utilizing the combination of the Rietveld method and the method of internal standard. The enter data were adopted from the Bruker Structural database and the internal standard was used for the amorphous phase quantification.

Results

Chlorides removal procedure

The chlorides content in the MW bottom ash and in the three samples of MSWI fly ash ranged from 2.62% to 14.1%. The results from the water leachate analysis are shown in Table 1. All samples had alkaline character. In the MSWI fly ash, chlorides were present in their soluble form as NaCl (15%), KCl (10%), $CaCl_2$ (51%) and as Friedel's salt ($Ca_2Al(OH)_6(Cl, OH) \cdot 2 H_2O$). The Friedel's salt presence is significant for the chloride capture in concrete and cement [13]. The maximum amount of chlorides washed away from the MW bottom ash and the MSWI fly ash was reached after one hour of leaching procedure (72.6% for the MW bottom ash and 81.8% for the MSWI fly ash). After two hours, 85.67% of chlorides from the MW bottom ash and 97.67% from the MSWI fly ash were leached. Finally after 24 hours, 93.61% of chlorides from the MW bottom ash and 98.5% from the MSWI fly ash were leached.

According to CSN EN 450-2, part 2 the concentration of chlorides < 0.1% is required for the bottom ash and fly ash utilisation as a construction material. This requirement was not achieved by the simple distilled water washing, due to the presence of the insoluble $BaCaCl_2$ form of chlorides in the bottom ash and fly ash. Ito et al. [13] showed that the most effective way for the insoluble chlorides removal from ashes was leaching

Tab. 2. Chloride content in the MW bottom ash and the MSWI fly ash before and after the chlorides removal procedure

Tab. 2. Zawartość chlorków w popiele dennym MO oraz popiele lotnym MOS przed i po procesie usuwania chlorków

Sample		Chloride content [%]		Leaching agent
		RAW	WASHED/LEACHED	
Fly ash	**1**	14.1	0.49	distilled water
	2	9.73	0.52	distilled water
	3	2,62	0.24	distilled water
Bottom ash		10.96	1.02	distilled water + 1M H_2SO_4

Tab. 4. CaO/SiO_2 ratio for the MW bottom ash and the MSWI fly ash samples

Tab. 4. Stosunek CaO/SiO_2 dla próbek popiołu dennego MO oraz popiołu lotnego MOS

Sample		CaO/SiO_2 ratio	
		RAW	WASHED/LEACHED
Fly ash	1	1.85	1.67
	2	0.75	1.00
	3	0.43	0.48
Bottom ash		1.62	-

with the sulphuric acid with pH < 4. Taking this into account, the three hours leaching procedure of the MW bottom ash was performed. A close to 99% removal of chlorides was observed with this procedure. The chloride content of the raw bottom and fly ash samples in comparison with the chloride content after the washing/leaching procedure is shown in Table 2.

None of the chlorides removal procedures were efficient to reach the chloride concentration limits (<0.1%) required for the utilisation of the MW bottom ash and the MSWI fly ash as a Portland cement replacement in concrete. The alternate solution may be the formation of the mixtures of MW bottom ash/MSWI fly ash with another kind of fly ash or quicklime, according to the technological requirements for solidification and strength rate of concrete or cement [10].

Mineralogical phase analysis

The results obtained from the mineralogical phase analysis of the raw (untreated) and washed/leached (treated) samples of MW bottom ash and the MSWI fly ashes are shown in Table 3. Differences in the mineralogical composition between the untreated and treated samples were observed. Specifically, all samples contained a large amount of amorphous phase (38.6% to 64.6% for raw samples and 33.06% - 56.13% for washed/leached samples). The greatest dissimilarity between the raw and washed/leached samples was observed regarding the crystallized minerals in the form of halite and sylvite. Mineralogical phase analysis confirmed the efficiency of the chlorides washing/leaching treatment, as zero content was observed for washed/leached samples. The results for the washed/leached samples are fairly consistent with the results obtained by [14, 15] who reported the presence of large amount of amorphous phase as well as the presence of halite, sylvite, calcite, quartz, gehlenite, anhydrite, aluminum, bassanite, feldspar, hematite, lime, perovskite, and titanite. Bayuseno et al. [16] also reported increases in the contents of calcite, quartz, anhydrite, ettringite and gehlenite in the washed fly ash sample and decreases in the contents of halite and sylvite. From the mineralogical phase analysis it can be also concluded that both MW bottom ash and MSWI fly ashes contain phases with pozzolanic/hydraulic properties. The presence of tricalcium aluminate (one of the most important phases in cement) was also observed in the bottom ash and fly ash by [17]. Akermanite and larnite/belite was identified in fly ash by [18].

The triangle diagram constructed from the chemical composition of the major oxides affect-

Tab. 3. XRD results of the raw and washed/leached MW bottom ash and the MSWI fly ash samples

Tab. 3. Wyniki XRD próbek popiołu dennego MO oraz popiołu lotnego MOS przed i po oczyszczaniu/ługowaniu

Mineralogical phase		**RAW [%]**				**WASHED/LEACHED [%]**			
		fly ash			**bottom ash**	**fly ash**			**bottom ash**
		1	**2**	**3**		**1**	**2**	**3**	
Halite	NaCl	11.98	9	2.43	9.67	-	-	-	-
Sylvite	KCl	6.92	4.28	-	-	-	-	-	-
Calcite	$CaCO_3$	10.96	11.39	6.84	1.95	15.61	15.16	11.89	15.86
Quartz	SiO_2	0.06	1.1	7.63	-	1.94	11.61	6.69	-
Periclase	MgO	1	-	-	-	2.34	2.80	1.61	-
Anhydrite	$CaSO_4$	5.74	3.68	2.61	1.79	6.79	4.97	2.05	-
Gehlenite	(C_2AS) $Ca_2Al(Si,Al)_2O_7$	8.06	6.79	6.58	-	10.82	11.24	9.55	5.90
Larnite	(C2S) Ca_2SiO_4	12.94	11.7	-	2.96	9.63	8.10	5.79	-
Belite	(β-C2S) Ca_2SiO_4	-	-	-	-	5.64	3.54	-	-
Hematite	Fe_2O_3	2,72	3,5	4,18	-	-	-	-	-
Sanidine	K(AlSi3O8)	-	-	2.44	-	-	-	-	-
Muscovite	$KAl_2(AlSi_3O_{10})(F,OH)_2$	-	-	2.71	-	-	-	-	-
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$	-	-	-	-	2.91	2.44	-	1.19
Tricalcium-Aluminate	(C3A) 3CaO·Al2O3	-	-	-	9.75	6.12	6.08	2.94	-
Albite	$NaAlSi_3O_8$	-	-	-	-	0.86	0.99	1.71	-
Microcline intermediate	$KAlSi_3O_8$	-	-	-	-	2.15	-	2.27	-
Aluminum	Al	-	-	-	-	1.239	7.63	2.74	-
Magnetite	Fe_3O_4	-	-	-	-	-	5.13	3.59	-
Zincite	ZnO	-	-	-	7.60	-	-	-	-
Mayenite	$12Ca0\cdot 7Al_2O_3$	-	-	-	2.32	-	-	-	5.14
Lime	CaO	2.19	-	-	0.93	-	-	-	-
Akermanite	$2CaO\cdot MgO\cdot 2SiO_2$	-	-	-	6.53	-	-	-	-
Merwinite	$Ca_3Mg(SiO_4)_2$	-	-	-	-	-	-	-	19.76
Ferrite	(C2F) Ca_3SiO_5	-	-	-	3.85	-	-	-	-
Amorphous		37.1	48.6	64.6	52.66	42.91	33.06	56.13	52.10
∑ pozzolanic properties		**28.93**	**22.17**	**9.19**	**25.41**	**41.91**	**36.37**	**20.33**	**30.80**

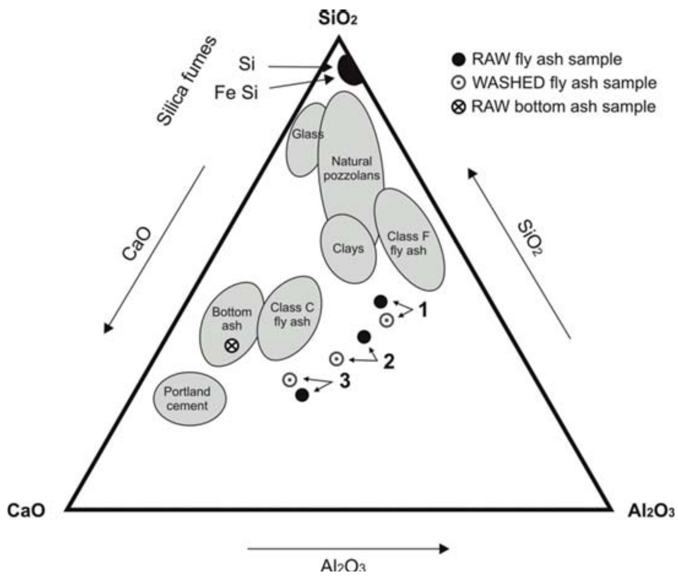

Fig. 1..Normalized diagram SiO_2–CaO–Al_2O_3 (silica fumes), modified from [19]

Rys. 1. Ynormalizowany diagram SiO_2-CaO-Al_2O_3 (opary dwutlenku krzemu), zmieniony od [19] ing pozzolanic properties (normalized at 100%) is shown in Fig. 1.sition of the projection points for the raw and washed MSWI fly ash samples, as well as for the raw MW bottom ash sample are presented. The pozzolanic/hydraulic properties of materials can be established from the CaO/SiO_2 ratio which magnitudes are presented in Table 4. The ratio in the range of 1-1.5 implies latent hydraulic properties, the ratio <0.5 suggests the pozzolanic properties and the ratio >2 indicates the hydraulic properties [19]. A considerable difference was observed in the CaO/SiO_2 ratio between the raw and washed/leached samples.

Conclusions

It is possible to efficiently remove chlorides from both, MW bottom ash and MSWI fly ash. Nevertheless, it is not possible to achieve the strict limiting factor of chloride content (<0.1%) for utilization of bottom and fly ash as a natural resource replacement in the construction industry by simple distilled water washing or combined water washing and acid leaching. The total sum of pozzolanic/hydraulic mineralogical phases increased after washing/leaching procedure in all studied samples. On the other hand, calcite was crystallized and the content of free lime decreased. Free lime has a considerable influence on the hydraulic/pozzolanic properties and the lack of this phase can be resolved by the addition of quicklime. Furthermore, it would also solve the problem of reaching the maximum chloride content limit for the utilization of bottom and fly ash in the construction industry. The influence of mineralogical phases change after washing/leaching treatment on the pozzolanic/hydraulic properties has to be further verified by strength test after Portland cement replacement in concrete.

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Usuwanie chlorków z pozostałości spopielenia odpadów

Chlorki zostały usunięte z próbek popiołu dennego odpadów medycznych oraz popiołu lotnego ze spopielenia miejskich odpadów stałych przy zastosowaniu procedur czyszczących/ługujących. Przeprowadzono dyskusje na temat procedur procesu, jak również analizy faz mineralogicznych próbek przed i po procesie oczyszczania/ługowania. Właściwości pucolaniczne/hydrauliczne próbek zostały określone i omówione w związku z wykorzystaniem popiołu dennego/lotnego.

Słowa kluczowe: popiół denny z odpadów medycznych, popiół lotny ze spopielenia miejskich odpadów stałych, oczyszczanie z chlorków, analiza fazy mineralogicznej